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AB	The Cu alloy comprises Cr 0.1-0.4, Zr .gtoreq.0 and <0.2, rare earth metal 0.002-0.2, Pb and/or Bi 0.002-0.2 wt.% (in total), and Cu bal. and the alloy has crystd. substances and deposited substances with diam. <3 .mu.m and crystal grain size <20 .mu.m. Alternatively, the above Cu alloy may also contain 0.01-1.0 wt.% Sn, Mg, Ni, Ag , Zn, Si, and/or Mn in total. The Cu alloy has high strength and cond. and is useful for lead frames for semiconductor device such as integrated circuit or for heat medium such as terminals, connectors, contacts, and so on.				

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(54) **Name of Invention:** Copper Alloy with Superior Stamping Traits for Electrical and Electronic Equipment

(57) **Summary**

Subject: To provide copper alloy equipped with such traits as strength and conductivity needed in such electrical and electronic equipment as leads, terminals and connectors, and thus a copper alloy with superior stamping traits for electrical and electronic equipment.

Means of Resolution: A copper alloy for electrical and electronic equipment with a content of Cr at 0.1~0.4wt%, Zr at up to 0.2wt% (including 0wt%), rare-earth elements at 0.002~0.2wt% and lead and/or bismuth totaling 0.002~0.2wt%,

and the remainder Cu and unavoidable impurities, and with the crystalline output and fragmented output* up to 3 μ m and crystal particles up to 20 μ m.

Scope of Patent Application

Application Item 1 A copper alloy for electrical and electronic equipment which has superior stamping traits and is characterized by containing Cr at 0.1~0.4wt%, Zr at up to 0.2wt% (including 0wt%), rare-earth elements at 0.002~0.2wt% and Pb and/or Bi at a total of 0.002~0.2wt%, and the remainder Cu and unavoidable impurities, with the size of the crystalline output and fragmented output up to 3 μ m and crystal particles up to 20 μ m.

Application Item 2 1 A copper alloy for electrical and electronic equipment which has superior stamping traits and is characterized by containing Cr at 0.1~0.4wt%, Zr at up to 0.2wt% (including 0wt%), rare-earth elements at 0.002~0.2wt% and Pb and/or Bi at a total of 0.002~0.2wt%, also one or more of Sn, Mg, Ni, Ag, Zn, Si and Mn at 0.1~1.0wt% and the remainder Cu and unavoidable impurities, with the size of the crystalline output and fragmented output up to 3 μ m in size and crystal particles up to 20 μ m.

Detailed Explanation of Invention

0001 Technical Field to Which Invention Belongs: This invention relates to a copper alloy applied to such electrical and electronic uses as leads, terminals, connectors, switches and electrodes, and especially bears on an electrical and electronic copper alloy suited to the semiconductor lead frame material of ICs, etc., wherein its stamping qualities are important.

0002 Usual Technology: For some time there has been wide use, in addition to iron materials, of plating materials such as noble metals (silver, lead, etc.) or solder on such copper materials as Cu-Sn, Cu-Fe, Cu-Cr or Cu-Cr-Zr, which have superior electrical and heat transmissivity, for the lead-frame material (one kind of lead material) terminal materials, etc., of semiconductor equipment. Yet, the copper materials used for such things as the above-noted

* Japanese terms rendered here as "crystalline output and fragmented output" appear in no reference source available to the translator, but are assumed from the meaning of the component characters.

lead frames are required to have strength, thermodurability, electrical and heat transmissivity, as well as affinity to plating with silver or solder, solder adherence, surface smoothness, the plated layer's resistance to heat

expansion, etc. Furthermore, it must have good etching qualities enabling high-precision shaping of such things as lead frames with their columns and surfaces, as well as good stamping qualities. Moreover, practicality from the cost aspect also is important.

The above required traits have become ever more rigorous in recent years in response to higher integration, higher capacity, miniaturization and price reductions in semiconductor devices. For instance, lead frames must become smaller, thinner, have more pins and be finer pitched, while matrix-format lead frames are being developed that are processed to have few pins but many rows. In making these lead frames, the stamping method has mainly been adopted for its superiority in precision of dimensions and for cost advantages. So, even more than previously, good stamping traits are required of the plate and bar materials for lead frames.

However, the following problems exist for stamping traits in the usual alloys of Cu-Cr systems or Cu-Cr-Zr systems:

- (1) During stamping they easily produce burrs and powder, which leave marks that degrade the bonding qualities or cause short circuits between leads,
- (2) They bend greatly during working, making dimension precision difficult to achieve,
- (3) The life of the stamping forms is short and their cost is high, etc.

Due to such things, we inventors we considered a variety of solutions to these problems and found that by adding to the copper matrix minute amounts of elements that crystallize out or fragment out as simple or compound chemicals the stamping traits could be improved. And, by doing further research we came to complete this invention.

0003 Problems Invention Seeks to Resolve: This invention has the goal of providing copper alloy for electrical and electronic equipment with such traits as the conductivity and strength needed for the copper alloy used for such electrical and electronic equipment as leads, terminals and connectors, and superior stamping qualities suited in particular to lead frames for such semiconductors as ICs.

0004 Means to Resolve Problems: The invention described in Application Item 1 is a copper alloy for electrical and electronic equipment with superior stamping qualities which is characterized by including Cr at 0.1~0.4wt%, Zr at up to 0.2wt% (including 0wt%), rare-earth elements at 0.002~0.2wt% and Pb and/or Bi totaling 0.002~0.2wt%, with the remainder Cu and unavoidable impurities, and with the size

of the crystalline output and fragmented output up to 3 μ m and crystal particles up to 20 μ m.

0005 The invention described in Application Item 2 is a copper alloy for electrical and electronic equipment which has superior stamping traits and is characterized by containing Cr at 0.1~0.4wt%, Zr up to 0.2wt% (including 0wt%), rare-earth elements at 0.002~ 0.2wt% and Pb and/or Bi totaling 0.002~0.2wt%, also one or more of Sn, Mg, Ni, Ag, Zn, Si and Mn at 0.1~1.0wt% and the remainder Cu and unavoidable impurities, with the crystalline output and fragmented output up to 3 μ m in size and crystal particles up to 20 μ m.

0006 Forms of Invention's Applications: Below we will explain the elements of this invention's alloy. The chrome is finely fragmented in the copper matrix and raises its strength without greatly lowering its conductivity. The reason for stipulating its content at 0.1~0.4wt% is that it does not produce its effects adequately at under 0.1wt%, and that at over 0.4wt% its effects are saturating and reduce conductivity. Also, the crystalline output and fragmented output become large and cause a drop in the resistance to heat expansion of the silver-plating layer, etc.

0007 Like the chrome, zirconium fragments finely in the copper matrix and raises its strength without much reducing the conductivity. The reason for stipulating its content at 0.2wt% or less (including 0wt%) is that above 0.2wt% its effects are saturating or reduce conductivity. Also, the crystalline output and fragmented output become large and cause a drop in resistance to heat swelling of the silver-plating layer, etc.

0008 The rare earth elements form compounds with the copper and crystallize or fragment in the copper matrix to improve the stamping qualities. The reason for stipulating a rare-earth element content of 0.002~0.2wt% is that at less than 0.002wt% its effects are not fully brought out, and that beyond 0.2wt% such defects as cracks are created during production-especially during heating or cooling-and reduce the throughput. Most desirable is 0.005~0.03wt%. For this rare earth, what is usually used is the low-cost misch metal (abbrev. MM) which combines lanthanum and cerium.

0009 The lead and bismuth crystallize or fragment out in the copper matrix and improve its stamping qualities. These elements are effective when added separately, but have a multiplier effect when added together. The reason for stipulating a total content of these elements of 0.002~

0.2wt% is the same as with rare earth elements. Stamping qualities are evaluated on three points: (1) shape and dimension precision of stamped ends and surfaces, (2) whether burrs are created, and (3) life of stamping forms. The above-noted rare earth elements mainly improve 1 and 2, while the Pb and Bi mainly improve 1 and 3. Hence, when the above-noted rare earth elements and the lead and/or bismuth are added in combination, a very large multiplier effect is attained.

0010 In this invention, the reason for stipulating a size of up to $3\mu\text{m}$ for the crystalline output or fragments of the compounds or single chemicals of the above-noted chrome, zirconium, rare-earth elements, lead, bismuth, etc., is that when they exceed $3\mu\text{m}$ in size the life of the metal molds is greatly shortened and the resistance of silver-plated layers to heat swelling is reduced, so that it loses suitability as a lead-frame material. In this invention, the reason that crystal particle size is stipulated at up to $20\mu\text{m}$ is that if crystal particle size exceeds that it cannot adequately produce the improved effect on stamping qualities due to the above-noted crystalline and fragment output.

0011 In this invention, the Sn, Mg, Ni, Ag, Zn, Si and Mn element groups contribute to raising the strength. Besides that, tin and nickel bring uniformly fine fragments, magnifying the effect of the chrome, while magnesium and manganese improve the hot-working qualities and resistance to hot flaking of the solder-plating layer formed on the surface. Silver and silicon keep coarse crystals from forming and improve bent-working and stamping qualities. The reason for stipulating a total content of these elements of 0.01~1.0wt% is that these effects are not adequately obtained at less than 0.01wt%, and above 1.0wt% conductivity drops off sharply.

0012 Besides the above-noted groups of elements, such groups as Co, Ti, Al, In, Te, Sr, Ba, Sb, Hf, Be, Fe, Nb, Pd, B and P have the effect of improving strength and heat resistance. The amount of such element groups added should be a range that will not greatly reduce conductivity. And, by holding the oxygen and sulfur admixed during casting to 50ppm or less, one can sustain at good levels the surface qualities that affect plating traits, solder adhesion, solder leakage, etc.

0013 By appropriate control of the content of prescribed alloying elements, the size of crystalline output and fragments and crystal granularity, this invention supports such

traits as needed strength and conductivity in material for electrical and electronic equipment such as lead frames and terminals, and so is a copper alloy for electrical and electronic equipment with improved stamping qualities. The copper alloy of this invention can be used not merely for ordinary rod or sheet material but also can be applied to use in unusual shapes with irregular cross sections.

0014 The method of manufacture recommended for this invention's copper alloy is, for example, casting in ingots by cooling the molten copper alloy with the prescribed components and proportions at 5°C/sec., working it while heated to 800~1000°C, quick-cooling the hot-worked material at a rate of 10°C/sec, then repeatedly cold-working and annealing by heating to 350~600°C for 30 seconds to 6 hours, after which it is cold-worked at a processing rate of 60% or less. With the above-noted processing conditions-i.e., manufacturing with the cooling rate during casting, the hot-working temperature, the cooling rate after hot-working-one can make the size of the crystalline output and fragments 3µm or less. Also, the conditions under which annealing is done between cold working--heating to 350~600°C for 30 seconds up to six hours are for beneficial lessening of processing warps and obtaining recrystallized structure in the crystal granules up to 20µm. Also, with the above-noted conditions for annealing, the size of the crystalline output and fragments is kept to within 3µm and yields good strength, conductivity and stamping qualities. This annealing may be done in a batching mode or as each is prepared.

0015 By annealing while recrystallizing at 200~500°C, the cold-worked material yielded by the above-noted method of manufacture has its internal stresses reduced and the dimension precision of the stamped material increased, while its drawing, bending and springy qualities are improved, giving it very suitable traits as a material for electrical and electronic equipment. The annealing process at this time also may be either by batch or as each is prepared. Finally, either before or after this annealing, or both before and after, if curing by a tension leveler, roller leveler, etc., is done, the stamping qualities will improve and one may get lead frame material, etc., with even better dimension precision.

0016 Application Examples: Below we will explain in greater detail application examples of this invention. In Application Example 1 we will describe applying the

invention's Application item 1, while in Application Example 2, we describe the invention's Application item 2.

Application Item 1: Alloys No. 1~5 shown in Table 1 were fused in a high-frequency fusing furnace and cast at a cooling rate of 6°C/sec to yield ingots 30mm thick, 100mm wide and 150mm long. For rare-earth elements we used MM (misch metal) with La and Ce the main components. Next we hot-rolled the above-noted ingots at 980° to a thickness of 12mm and immediately cooled them at a rate of 30°C/sec. We next shaved their surfaces to remove the oxide coating, getting them down to 9mm. Then we cold-rolled them down to 1.2mm thickness and annealed them in an inert-gas environment for one hour at 540°C, then cold-rolled them to a thickness of 0.33mm and annealed them in an inert-gas environment at 540°C for one hour. We then did a finish rolling down to 0.2mm thick and completed the manufacture of the material by annealing for 2 hours in an environment of inert-gas at 300°C.

0017 Comparative Example 1: Using the alloys shown as Nos. 16~22, 25 and 31 in Table 1, we fabricated the flat material just as with Application Example 1. The alloy makeup of comparative example Nos. 16-22 are outside of this invention's stipulations; No. 25 was annealed at a high temperature to make the crystal granules large, while No. 31 was cooled slowly during casting to make the crystal output large.

0018 With each of the plate materials thus obtained, we measured the size of the crystal output and fragments and the crystal granule size. We also tested their tensile strength, conductivity, the silver-plated layer's resistance to heat expansion, and the stamping qualities. In Table 1 are shown alloy composition, diameters of the crystalline output and crystalline granularity. The research results are shown in Table 2. The lead, bismuth and rare-earth elements are shown as the first additive group. Below we will describe our measuring and testing methods.

- (1) Size of crystal output and fragments: We used a scanning electron microscope (1000X) to measure maximum diameters of these and took the averages of 10 each.
- (2) Size of crystal grains: Using an optical microscope (200X) with the JIS-H0501 standard, we did measurements by the sectioning method.
- (3) Tensile strength: We measured according to JIS-Z2241.
- (4) Conductivity: We measured according to JIS-Z0505.

(5) Ag-plated layer's resistance to heat expansion: After electrolytic skimming of a 40mmX100mm test piece, we did an acid wash with a 10% sulfuric acid solution and electro-plated silver 5 μ m thick in a cyanic bath, heated this in the atmosphere for 10 minutes at 450°C and then inspected the surface with an optical microscope (20X) for the presence of swelling. We judged it failed when the inspection clearly revealed swelling, and passed when that was not the case.

(6) Stamping traits: We used an SKD11 metal form to open a rectangular hole of 1mmx5mm, randomly selected 20 samples from the stampings from the 5001st to the 10,000th time and measured the size of these samples' burrs (burr height H₁). We also inspected the stamped surfaces, measured thickness **a** of fragments and found their ratio to thickness **b** of test fragments [(a/b)X100%]. We made this fragment ratio one measure of the stamping traits, saying that the larger this value was, the better the stamping traits. I.e., we judged that precision processing could be done when the throughput is high. Furthermore, as to the life of the metal forms, after repolishing the metal forms, we randomly selected 20 samples from the 50,001st time through the 55,000th time and evaluated them by measuring the size of their burrs (burr height H₂). The greater the difference between this burr height H₂ and burr height H₁, the more severe the wear on the metal form had been. When form wear is severe, the time required for repolishing increases. Productivity drops and metal form costs go up.

0019 Table 1

Examples of This Invention

No.	Cr	Zr	1 st group added elements	wt%	Diameters of crystals &	
<u>precipitates</u>						
			Particle size			
1	0.15	--	Bi	0.005 MM	0.009	0.6 10
2	0.24	--	Pb	0.11 MM	0.02	1.5 10
3	0.33	--	Bi	0.03	Pb	0.007 MM 0.05 2.2
4	0.25	0.04	Pb	0.02 MM	0.12	1.4 10
5	0.25	0.13	Bi	0.005	Pb	0.03
6	0.02	1.7	10	<u>Comparative Examples</u>		
7	0.04	0.3	10	16	0.05	-- Pb 0.01 MM
8	0.44	--	Bi	0.01 MM	0.01	3.8 10
9	0.25	0.24	Bi	0.005	Pb	0.005 MM 0.01 3.3 10
10	0.25	--	Pb	0.001	MM	0.02 0.9 10
11	0.24	0.09	Bi	0.01	MM	0.001 1.7 10
12	0.24	--	Bi	0.08	Pb	0.15 MM
13	0.01	Fabrication halted due to heating cracks --				22 0.25 0.10 Bi 0.01
14	Pb	0.03	MM	0.23	Ditto	--
15	0.25	--	Pb	0.10	MM	0.02 1.4 30
16	0.24	0.09	Bi	0.01	MM	0.01 3.2 10
17						31

Note: (1) Crystal output and fragments' maximum average diameter: μ m. (2) Crystal particle size: μ m

0020 Table 2**This Invention's Examples**

No.	Tensile Strength N/mm ₂	Conduc- tivity % IACS	Ag			
layer resistnc to heat swelling	Burr height H ₁ in mm	Ratio				
of cut part in %	Burr height H ₂ in mm					
1	401	88	Good	0.005	55	0.008
2	435	83	"	0.001	69	0.003
3	453	80	"	0.001	71	0.005
4	446	81	"	0.003	64	0.005
5	461	80	"	0.002	67	0.004
Comparative	Examples					
16	362	92	Good	0.006	52	0.009
17	470	78	Poor	0.005	57	0.010
18	488	76	Poor	0.003	64	0.009
19	441	83	Good	0.012	40	0.020
20	457	81	Good	0.014	38	0.021
21 22	Fabrication	halted due	to cracks	during heat processing		
25	426	82	Good	0.006	49	0.014
31	479	72	Poor	0.001	71	0.008

0021 As is clear from Table 2, this invention's Nos. 1~5 all showed superior traits. On the other hand, comparative example No. 16 had less strength due to the small amount of chrome. Comparative examples 17 and 18 had more fragments because the amount of zirconium was high; had swelling of the silver-plated layer and more difference between the burrs' H₁ and H₂ heights. So, abrasion of the metal molds was severe. Comparative examples 19 and 20 had less of the first-group additive elements, so that burr heights H₁ and H₂ were high and the ratio of the cut part was small. In short, their stamping traits were worse. With greater amounts of first-group additive elements in Nos. 21 and 22, cracks appeared during hot and cold working and fabrication was halted. Since we made the annealing temperature high for No. 25, its crystal particle size was large and stamping traits had worsened. And, because the cooling rate during casting of No. 31 was slowed down, the crystalline output was coarsened, the silver-plated layer had heat swelling and wear on the metal molds was severe.

0022 Application Example 2: Other than using the alloys of Nos. 6~15 shown in Table 3, we fabricated the flat material the same way as with Application Example 1.

0023 Comparative Examples 2: Other than using the alloys of Nos. 23, 24, 26 and 32 shown in Table 4, we made the flat material the same way as Application Example 1. Nos. 23 and 24 had second additive-group elements falling outside the stipulations of this invention. Comparative Example No.

32 was annealed at a high temperature to make its crystalline particles large. And, No. 26 was cooled at a slow rate during casting to make its crystal output large. We measured the flat material thus obtained for size of crystalline output and fragments and crystal particle size. We also used the same methods as with Application Example 1 to test each sample's tensile strength, conductivity, resistance to heat swelling of the silver-plated layer and stamping properties required for lead frames. We used the same methods as with Application Example 1 to measure and test. The results are shown in Tables 5 and 6. We show also in Table 3 the diameters of the crystal output and crystal particle sizes.

0024 Table 3: This Invention's Examples

No.	Cr	Zr	1 st Add' ve Group//2 nd Additive
Group wt%	Fragmented Crystal		Particle size
6	0.25	--	Bi 0.02 Pb 0.01 MM 0.04// Sn
0.23	1.0	10	
7	0.24	--	Pb 0.01 MM 0.03// Mg 0.12 Ni
0.21	0.8	10	
8	0.23	--	Bi 0.009 MM 0.08// Ag 0.56 Si
0.11 Mn 0.05		1.3	10
9	0.25	--	Bi 0.007 Pb 0.03 MM 0.02// Sn
0.08 Zn 0.09		1.1	10
10	0.25	--	Pb 0.02 MM 0.007// Sn 0.21 Zn
0.22	0.9	10	
11	0.25	0.07	Bi 0.01 MM 0.06// Sn 0.36 Zn
0.40	1.3	10	
12	0.24	0.06	Bi 0.01 Pb 0.06 MM 0.03// Ag
0.22	1.1	10	
13	0.26	0.08	Bi 0.009 Pb 0.008 MM 0.01// Mg
0.05 Si 0.03		1.5	10
14	0.24	0.09	Pb 0.02 MM 0.02// Mg 0.18 Si
0.10	1.4	10	
15	0.25	0.11	Bi 0.01 Pb 0.005 MM 0.07// Ni
0.27 Sn 0.07 Mn 0.11		1.7	10

Notes: (1) Average of maximum diameters of crystal output and precipitates: μm . (2) Crystal particle size: μm .

0025 Table 4
Comparative Examples

No.	Cr	Zr	1 st Additive Group//2 nd Additive
Group wt%	Precipi- tates		Particle size
23	0.24	--	Bi 0.01 Pb 0.01 MM 0.02// Mg 1.4
	1.0	10	
24	0.25	0.07	Bi 0.01 MM 0.03// Sn 0.35 Ni
0.45 Mn 0.23		1.6	10
32	0.25	--	Pb 0.10 MM 0.02// Zn 0.22 1.4
	30		
26	0.24	0.17	Bi 0.009 Pb 0.03 MM 0.10// Ag
0.11 Zn 0.75		3.2	10

Notes: (1) Average of maximum diameters of crystal output and precipitates: μm . (2) Crystal particle size: μm .

0026 Table 5

No.	Tensile Strength N/mm ²			Conduc- tivity % IACS Ag		
	layer resistnc to heat swelling			Burr height H ₁ in mm		
	of cut part in %	Burr height H ₂ in mm				Ratio
6	507	78	Good	0.002	68	0.003
7	488	67	"	0.004	60	0.006
8	520	71	"	0.003	63	0.006
9	493	80	"	0.002	66	0.004

0027 Table 6

No.	Tensile Strength N/mm ²			Conduc- tivity % IACS Ag		
	layer resistnc to heat swelling			Burr height H ₁ in mm		
	of cut part in %	Burr height H ₂ in mm				Ratio
10	513	76	Good	0.005	57	0.007
11	534	64	"	0.003	63	0.006
12	458	79	"	0.003	64	0.005
13	470	78	"	0.003	62	0.005
14	487	65	"	0.004	59	0.007
15	531	63	"	0.002	67	0.003
Comparative	Examples					
23	503	52	Good	0.002	67	0.004
24	564	47	"	0.004	58	0.007
32	426	82	"	0.006	49	0.014
26	479	72	Poor	0.001	71	0.008

0028 As will be seen from Tables 5 and 6, This invention's Nos. 6~15 all show superior traits, and especially their tensile strength has been improved overall compared to Application Example 1. This is because they contain the second-group additive elements. Also, Nos. 6, 9~11 and 15, which have proper amounts of tin and zinc added, have an excellent balance of stamping traits. In contrast, comparative cases Nos. 23 and 24 have reduced conductivity due to too much of the second-group elements being added. And, No. 32 had large crystal particle sizes because of our making the annealing temperature high, so that the stamping traits had worsened. Also, because No. 26 had been cooled at a slow rate during casting, its crystalline output was coarse and the silver-plated layer had heat swelling. Also, wear on the metal molds was severe.

0029 **Effectiveness of Invention:** As discussed above, this invention's copper alloy for electrical and electronic equipment has strength and conductivity equal to that of the usual Cu-Cr alloys or Cu-Cr-Zr alloys, and its stamping qualities have been broadly improved. So, it is especially

suited to semiconductor lead frames such as for ICs in which there is emphasis on stamping qualities, and can well meet the needs of higher integration, miniaturization and cost reduction. Also, besides the above-mentioned lead frames, it can well be applied to such uses as relays, terminals, connectors and switches and even to general conductor materials or hot media such as heat sinks. So, it has marked industrial utility.